

# A Brief Review on Results and Computational Algorithms for Minimizing the Lennard-Jones Potential

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## Abstract

The Lennard-Jones (LJ) Potential Energy Problem is to construct the most stable form of  $N$  atoms of a molecule with the minimal LJ potential energy. This problem has a simple mathematical form

$$\text{minimize } f(x) = 4 \sum_{i=1}^N \sum_{j=1, j < i}^N \left( \frac{1}{\tau_{ij}^6} - \frac{1}{\tau_{ij}^3} \right) \quad \text{subject to } x \in \mathbb{R}^n,$$

where  $\tau_{ij} = (x_{3i-2} - x_{3j-2})^2 + (x_{3i-1} - x_{3j-1})^2 + (x_{3i} - x_{3j})^2$ ,  $(x_{3i-2}, x_{3i-1}, x_{3i})$  is the coordinates of atom  $i$  in  $\mathbb{R}^3$ ,  $i, j = 1, 2, \dots, N (\geq 2 \text{ integer})$ , and  $n = 3N$ ; however it is a challenging and difficult problem for many optimization methods when  $N$  is larger. In this paper, a brief review and a bibliography of important computational algorithms on minimizing the LJ potential energy are introduced in Sections 1 and 2. Section 3 of this paper illuminates many beautiful graphs (gotten by the author nearly 10 years ago) for the three dimensional structures of molecules with minimal LJ potential.

## 1 Introduction

the Lennard-Jones potential energy problem is to construct the most stable form of  $N$  atoms of some material with the minimal energy structure. Its form in mathematics is very simple:

$$\text{minimize } f(x) = 4 \sum_{i=1}^N \sum_{j=1, j < i}^N \left( \frac{1}{\tau_{ij}^6} - \frac{1}{\tau_{ij}^3} \right) \quad \text{subject to } x \in \mathbb{R}^n, \quad (1)$$

where  $\tau_{ij} = (x_{3i-2} - x_{3j-2})^2 + (x_{3i-1} - x_{3j-1})^2 + (x_{3i} - x_{3j})^2$ ,  $(x_{3i-2}, x_{3i-1}, x_{3i}) \in \mathbb{R}^3$  is the coordinates of atom  $i$ ,  $i, j = 1, 2, \dots, N (\geq 2 \text{ integer})$ , and  $n = 3N$ . However, it interests many researchers in the field of biology, physics, chemistry, mathematical optimization, computer science, and materials science. The reason lies in the nonconvexity of the objective function and the huge number of local minima, which is growing exponentially with  $N$ . [22] tells us the number of distinct local minima of  $N$ -atoms Lennard-Jones problem is about  $O(e^{N^2})$ . For example, When  $N = 6, 7, 8, 9, 10, 11, 12, 13$  the numbers of distinct local minima of the problem are 2, 4, 8, 18, 57, 145,

366, 988 respectively ([26]). From the point of view of numerical optimization methods, this problem is an excellent test problem for local or global optimization methods. However, the Lennard-Jones Problem is very difficult and challenging to many optimization methods even when  $N$  is not very large. By now, the best objective function values for  $2 \leq N \leq 309$  [49, 50, 51] are well known. At first, around 1972 Hoare and Pal [23, 24, 25] gave the best values for atoms 5~16, 18~21, 25, 26, 29, 55. Then, in 1987, Northby ([35]) made a landmark—yielding most of the lowest values in the range  $13 \leq N \leq 150$ ; and in 1999 [39] presented the best results on  $151 \leq N \leq 309$  with the exception of  $N=192$ , 201 [43],  $N=200$ , 300 [46],  $N=185$  [31],  $N=186$ , 187 [19]. At present, about thirty percent of Northby’s results have been improved [46, 12, 13, 32, 16, 15, 44, 9, 11, 45]. The improvements are described as follows. In 1994 Xue ([46]) got the best values for  $N=65,66,134$ . Doye et al ([12, 13]) in 1995 gave the best values on  $N=38,75\sim77,102\sim104$ ; and Leary in 1997 ([32]) presented best values for  $N=69,78,88,107,113,115$ . Wolf ([45]) got the best values on  $N=82, 84, 86, 88, 92, 93, 94, 95, 96, 99, 100$  in 1998. For the left so-called magic numbers sequence: 17,23,24,72,88, Freeman, Farges, Wille, Coleman, Deaven ([16, 15, 44, 9, 11]) got the best results, respectively.

The outline of this paper is as follows. In section 2, we review the methods in the most important references above-mentioned. Section 3 contains a description of our techniques and methods to tackle problem (1); and results of numerical experiments for the problem are given in this section. The structure of our optimal solutions is illustrated, and can be compared with those of others, at the end of this section. Section 4 concludes the paper.

## 2 Approaches to the Lennard-Jones Problem

Some good summaries on the methods solving the Lennard-Jones problem in fact can be found in [35, 14, 36, 18, 32]. In this section we review the methods in the most important references [23, 24, 25, 35, 39, 43, 46, 31, 19, 12, 13, 32, 45, 16, 15, 44, 9, 11].

Hoare and Pal’s work ([23, 24, 25]) may be the early most successful results on Lennard-Jones problem. The idea is using build-up technique to construct the initial solutions which are expected to represent low energy states, and using those initial solutions as starting points for a local search method to relax to the optimal solution ([25]). The starting seed is the regular unit tetrahedron with atoms at the vertices, the obvious global optimal solution for  $N=4$ . Beginning with this tetrahedron, Hoare and Pal added one atom at a time to construct a sequence of polytetrahedral structures and at last got good results up to  $N=66$ . For example, for  $N=5$  its globally optimal trigonal bi-pyramid (bi-tetrahedron) structure is gotten by adding an atom at the tetrahedral capping position over a triangular face; following the bi-tetrahedron structure, the optimal structure of  $N=6$  is tri-tetrahedron (another known optimal structure for  $N=6$  is octahedron (using tetrahedral capping over triangular faces and half-octahedral capping over square faces), which is not a polytetrahedron); for  $N=7$  its best structure constructed is the pentagonal bi-pyramid, a structure with a five-fold axis of symmetry. Many computer science data structure procedures such as greedy forward growth operator and reverse greedy operator can make the build-up technique

work well. [23] describes the application of methods of studying noncrystalline clusters to the study of “spherical” face centred cubic (fcc) microcrystallites. [24] describes the chief geometrical features of the clustering of small numbers of interacting particles.

The data structure of Northby ([35]) in finding the good starting solution is the lattice based structure. The lattice structures consist of an icosahedral core and particular combinations of surface lattice points. [34] first constructed a class of icosahedral packings by adding successively larger icosahedral shells in layers around a core central atom; this icosahedral lattice can be described as 20 slightly flattened tetrahedrally shaped fcc units with 12 vertices on a sphere centered at the core atom. Atoms within each triangular face are placed in staggered rows in a two dimensional hexagonal close-packed arrangement. Each atom in the interior of a face in a given shell is a tetrahedral capping position relative to three atoms in the underlying shell. Northby relaxed the structure of [34] to get his IC and FC multilayer icosahedral lattice structures. The IC lattice can be referred to the FORTRAN code in [46]; it consists of all those sites which will comprise the outer shell of the next complete Mackay ([34]) icosahedron. FC lattice is a slight modification of IC lattice in that its outer shell maintains icosahedral symmetry and consists of points at the icosahedral vertices and the stacking fault positions of the outer IC shell. Basing on the IC and FC lattices, Northy gave his algorithm first finding a set of lattice local minimizers and then relaxing those lattice minimizers by performing continuous minimization starting with those lattice minimizers. The algorithm was summarized as Algorithm 1 and Algorithm 2 of [46].

The great majority of the best known solutions of Northy are icosahedral in character. The hybridization of global search and local search methods, usually, is more effective to solve the large scale problem than the global search method or local search method working alone. Catching those two ideas, [39] combined a genetic algorithm with a stochastic search procedure on icosahedrally derived lattices. The structures of the optimal solutions gotten in [39] are either icosahedral or decahedral in character. The best results of [45] for  $N = 82, 84, 86, 88, 92, 93, 94, 95, 96, 99, 100$  were gotten by using a genetic algorithm alone. Deaven et al ([11]) also using the genetic algorithm got the optimal value known for the magic number  $N = 88$ .

The successful works to improve Northby’s results ([35]) were mainly done by Xue ([46]), Leary ([32]), and Doye et al ([12, 13]).

Xue ([46]) introduced a modified version of the Northby algorithm. He showed that in some cases the relaxation of the outer shell lattice local minimizer with a worse potential function value may lead to a local minimizer with a better value. In Northby’s algorithm the lattice search part is a discrete optimization local search procedure, which makes a lattice move to its neighboring lattice with  $O(N^{\frac{2}{3}})$  time complexity. In [47] Xue introduced a simple storage data structure to reduce the time complexity to  $O(N^{\frac{2}{3}})$  per move; and then used a two-level simulated annealing algorithm within the supercomputer CM-5 to be able to solve fastly the Lennard-Jones problem with sizes as large as 100,000 atoms. In [46] by employing AVL trees ([27]) data structure Xue furthermore reduced the time complexity to  $O(\log N)$  if NN (nearest neighbor) potential function is used. He ([46]) relaxed *every* lattice local minimizer found instead of relaxing only those lattice local minimizers with best known potential function value by a powerful Truncated Newton local search method, and at last got the best results known for  $N = 65, 66, 134, 200, 300$ .

Leary ([32]) gave a successful Big Bang Algorithm in 1997 for getting the best values known of  $N = 69, 78, 88, 107, 113, 115$ . In [32] the FCC lattice structure is discussed and its connections are made with the macrocluster problem. It is also concluded in [32] that almost all known exceptions to global optimality of the well-known Northby multilayer icosahedral conformations for microclusters are shown to be minor variants of that geometry. The Big Bang Algorithm contains 3 steps: Step 1 is an initial solution generating procedure which randomly generates each coordinate of the initial solution with the independently normal distribution; Step 2 is to generate the new neighborhood solution by discrete-typed fixed step steepest descent method, which is repeated until no further progress is made; Step 3 is to relax the best solution gotten in Step 2 by a continuous optimization method—conjugate gradient method.

Doye et al ([12]) investigated the structures of clusters by mapping the structure of the global minimum as a function of both cluster size and the range of the pair potential which is appropriate to the clusters of diatomic molecule,  $C_{60}$  molecule, and the ones between them both. For the larger clusters the structure of the global minimum changes from icosahedral to decahedral to fcc as the range is decreased ([12]). In [13] Doye et al predicted the growth sequences for small decahedral and fcc clusters by maximisation of the number of NN contacts.

Lastly, in this section, we give a brief review of methods on the magic numbers  $N = 17, 23, 24, 72, 88$  and on the exceptions to [39]. Freeman et al ([16]) presented the best value for  $N = 17$  when the thermodynamic properties of argon clusters were studied by a combination of classical and quantum Monte Carlo methods. The poly-icosahedral growth of Farges et al ([15]) starts from a 13-atom primitive icosahedron containing a central atom and 12 surface atoms. On each one of the five tetrahedral sites, surrounding a particular vertex, a new atom is added and finally a sixth atom is placed on top to create a pentagonal cap. In this way a 19-atom structure being made of double interpenetrating icosahedra, which is a 13-atom icosahedra sharing 9 atoms, is obtained. I.e., for three pentagonal bipyramids each one shares an apex with its nearest neighbour. In this way a 23-atom model consisting of three interpenetrating icosahedra is gotten for the best value known. Wille ([44]) used the simulated annealing method yielding low-lying energy states whose distribution depends on the cooling rate to find the best solution known for  $N = 24$ . Coleman et al ([9]) proposed a build-up process to construct the optimal solution structures. The HOC (half octahedral cap) structure of the optimal solution for  $N = 72$  is found by a prototype algorithm designed using the anisotropic effective energy simulated annealing method at each build-up stage ([9]). Wales and Doye ([43]) in 1997 gave the lowest values known for  $N = 192, 201$ . Their method is so-called basin-hopping method, in which first the transformed function  $\tilde{f}(x) = \min\{f(x)\}$  was defined and performed starting from  $x$  by the PR conjugate gradient method (see, for example, [42]), and then the energy landscape for the function  $\tilde{f}(x)$  was explored using a canonical Monte Carlo simulation. Leary ([31]) has developed techniques for moving along sequences of local minima with decreasing energies to arrive at good candidates for global optima and got the best value known on  $N = 185$ .

### 3 Our approach to the Lennard-Jones Problem

In this section we first briefly introduce the discrete gradient method; then present a hybrid discrete gradient and simulated annealing method. And then we give some techniques, with the discrete gradient method and the hybrid method, to tackle the Lennard-Jones Problem.

#### 3.1 Discrete Gradient Method

Discrete gradient method is a derivative-free local search method for nonsmooth optimization ([3, 4]). Results of numerical experiments presented in [5] show that this method can jump over stationary points, which are not local minima, so we can reduce the number of stationary points, which we meet. Details of this method can be found, for example, in [3, 4].

#### 3.2 Hybrid Discrete Gradient and Simulated Annealing Method

Simulated annealing method is a global search method. It has received a great deal of attention in last several years. First, this method was applied to combinatorial optimization, i.e. when the objective function is defined in a discrete domain (see [8, 30]). Later this method was applied to solve continuous global optimization problems (see [7, 10, 29, 33, 38]). Convergence of simulated annealing method is studied, for example, in [33].

Numerical experiments show that algorithms based on a combination of the global and local search techniques are more effective than the global search methods working alone (see, for example, [5, 48, 20]). In these methods a local search algorithm is used to find a stationary point and a global search algorithm is used to escape from this stationary point and to find a new starting point for a local search algorithm. In this subsection, we develop a new hybrid simulated annealing and discrete gradient method. During the whole process of the method, both simulated annealing and discrete gradient methods need the the objective function values only.

The simulated annealing method for solving continuous global optimization problems was studied by many authors (see, for example, [7, 10, 29, 33, 38]). *Neighborhood solution search* procedure is one of the important steps in this method. Noticing that the neighborhood solution search for simulated annealing method should be at least based on two basic ideas: (a) neighbor means “nearby”, (b) simulated annealing method is a stochastic method so that the neighborhood solution should be randomly taken, we may simply give a neighborhood solution search procedure for simulated annealing algorithm:

Uniformly randomly keeping  $n - 1$  coordinates of  $x$ , and making the left one coordinate of  $x$  randomly take a value such that the new solution  $x'$  still feasible. This gives  $x'$ .

When the feasible region of the optimization problem is the unit simplex  $S = \{x \in \mathbb{R}_+^n : \sum_{i=1}^n x_i = 1\}$ , the neighborhood solution search procedure should be done a little modification:

Uniformly randomly keeping  $n - 2$  coordinates of  $x$ , and making one coordinate from the two elements left to  $x$  randomly take a value from  $[0,1]$  such that the value of the sum of the  $n - 1$  coordinates gotten not greater than 1. Another left coordinate of  $x'$  is given the value 1-sum. This gives  $x'$ .

The hybrid method starts from an initial point, first executes discrete gradient method to find local minimum, then carries on simulated annealing method in order to escape from this local minimum and to find a new starting point for the discrete gradient method. Then we again apply the discrete gradient method starting from the last point and so on until the sequence of the optimal objective function values gotten is convergent. The pseudo-code of the hybrid method is listed as following:

**Algorithm 1:** Hybrid simulated annealing and discrete gradient method

**Initialization:**

*Define the objective function  $f$  and its feasible solution space.*

*Call the initial feasible solution generating procedure to get  $x$ .*

*Call initial temperature selecting procedure to get  $T$ .*

*Initialization of  $f$ :  $f = f(x)$ .*

*Initialize the neighbourhood feasible solution:  $x\_neighbour = 0$ .*

*Initialize  $x\_best$ :  $x\_best = x$ .*

*Initialize  $f\_best$ :  $f\_best = f$ .*

do {

**Discrete Gradient local search part:**

*$f\_best\_local = \text{local\_search}(x\_best, x\_new\_gotten);$*

*$x = x\_new\_gotten;$*

**Simulated Annealing global search part:**

do {

do {

*$x\_neighbour = \text{randomly\_perturb}(x);$*

*$f\_neighbour = f(x\_neighbour);$*

*Calculate the difference  $\Delta = f\_neighbour - f;$*

**If** ( $\Delta \leq 0$ ) **or** ( $\text{random}[0,1] < \exp(-\Delta/T)$ )

*$x = x\_neighbour$   $f = f\_neighbour;$*

**If** ( $f \leq f\_best$ )  $x\_best = x$   $f\_best = f;$

**}** while (equilibrium has not been reached);

Temperature annealing

**}** while (Simulated Annealing stop criterion has not been met);

**}** while ( $f\_best - f\_best\_local \leq -0.001$ );

The convergence of the proposed hybrid method directly follows from the convergence of the simulated annealing and the discrete gradient methods.

The simulated annealing method part consists of two procedures: inner procedure for the search of neighborhood solution and outer procedure for the cooling temperature  $T$ . The number of iterations of inner and outer loops are taken to be large enough for guaranteeing that the sufficient iterations will be carried on to escape from the current

local minimum. In implementing the hybrid method, we use  $T = 0.9 * T$  as the temperature annealing schedule and the initial temperature is taken large enough according to the rule in [30]. We restrict the number of iterations for the outer procedure by 100 and number of iterations for the inner procedure by 1000. The discrete gradient method part is terminated when the distance between the approximation to the subdifferential and origin is less than a given tolerance  $\epsilon > 0$  ( $\epsilon = 10^{-4}$ ).

### 3.3 Minimization of Lennard-Jones potential function

In this subsection, the proposed discrete gradient method and hybrid discrete gradient and simulated annealing method, with the techniques given in the below, have been applied for minimization of well-known Lennard-Jones potential function in protein folding problem (1). The nonconvex Lennard-Jones potential function has a huge number of local minima. Therefore many global optimization techniques fail to minimize it. The proposed hybrid method fails to solve this problem when number of atoms  $N \geq 20$ . In order to reduce the number of local minima we suggest to approximate the function

$$\varphi(\tau) = \frac{1}{\tau^6} - \frac{1}{\tau^3}$$

by the following function:

$$g(\tau) = \max(g_1(\tau), \min(g_2(\tau), g_3(\tau)))$$

where  $g_1(\tau)$  is the piecewise linear approximation of the function  $\varphi(\tau)$  in segment  $(0, r_0]$ ,  $g_2(\tau)$  is the piecewise linear approximation of this function over segment  $[r_0, r_1]$ , and finally  $g_3(\tau)$  is the piecewise linear approximation over  $[r_1, b]$  and  $b$  is large enough number. Here

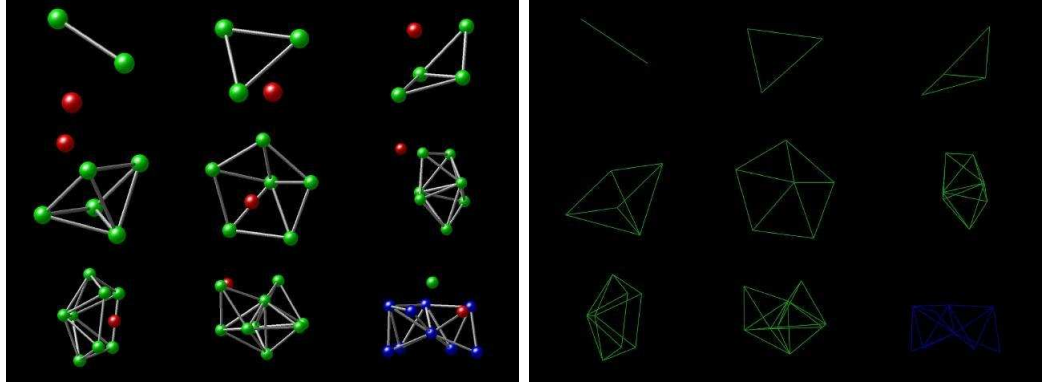
$$r_0 = \sqrt[3]{2}, \quad r_1 = 1/\sqrt[3]{2/7}$$

Such a approximation of the function  $\varphi(\tau)$  allows us to remove many local minima of the Lennard-Jones potential function and to get a good approximation to the global minimum of the objective function  $f$  in problem (1).

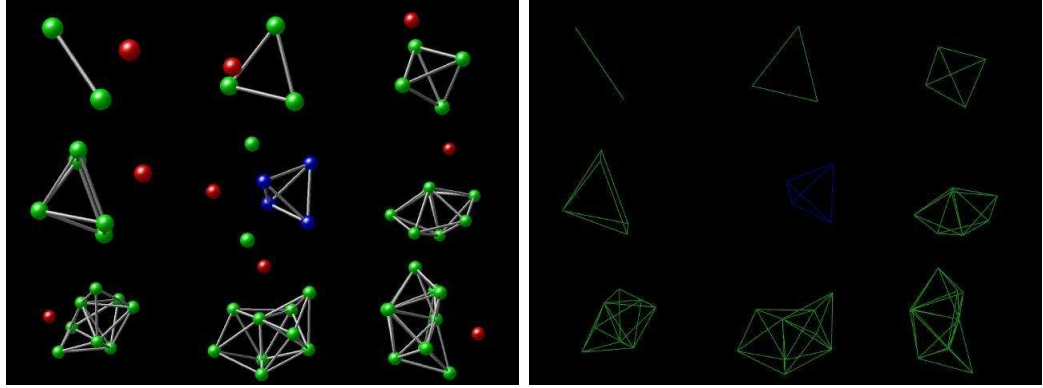
In numerical experiments we take  $b = 16$  and divide the segment  $[0.001, r_0]$  into 100 segments, the segment  $[r_0, r_1]$  into 100 segments and the  $[r_1, 16]$  into 50 segments which allows one to get good approximations for the function  $\varphi(\tau)$ . The replacement of the function  $\varphi(\tau)$  by the function  $g(\tau)$  makes the objective function nonsmooth. On the other side such a replacement significantly reduce the number of local minima. Since the discrete gradient method is a method of nonsmooth optimization the proposed hybrid method can be applied for solving this transformed problem.

When solving the Lennard-Jones problem, first we use the discrete gradient method with build-up technique to relax to an initial solution. Then we apply the hybrid discrete gradient and simulated annealing method, with the good approximation for the objective function, to get another initial solution. Starting from this initial solution we again apply the derivative-free discrete gradient method and at last get the global solution. Results of numerical experiments are presented in Table 1 as the appendix. Results from Table 1 show that our techniques and methods effectively solve protein folding problem when number of atoms is not greater than 310.

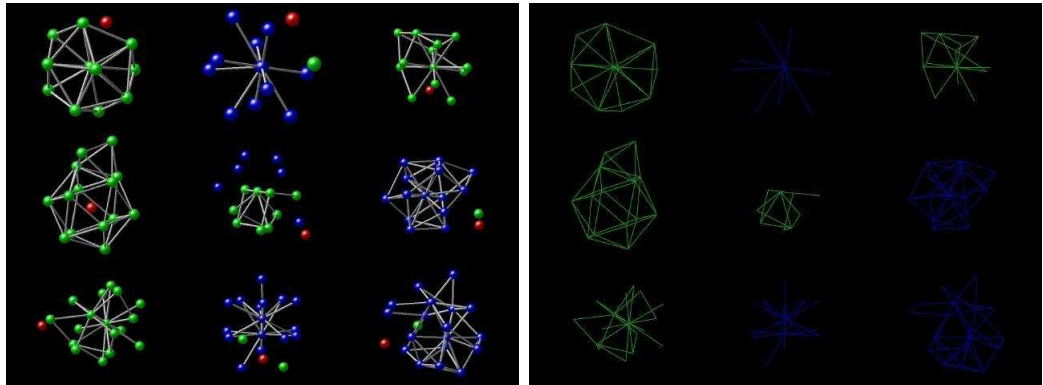
The structure of the optimal solutions corresponding to the above optimal values is illustrated and can be compared with the ones of [49, 39] in the following figures:



N=3, 4, 5, 6, 7, 8, 9, 10, 11 (ours)

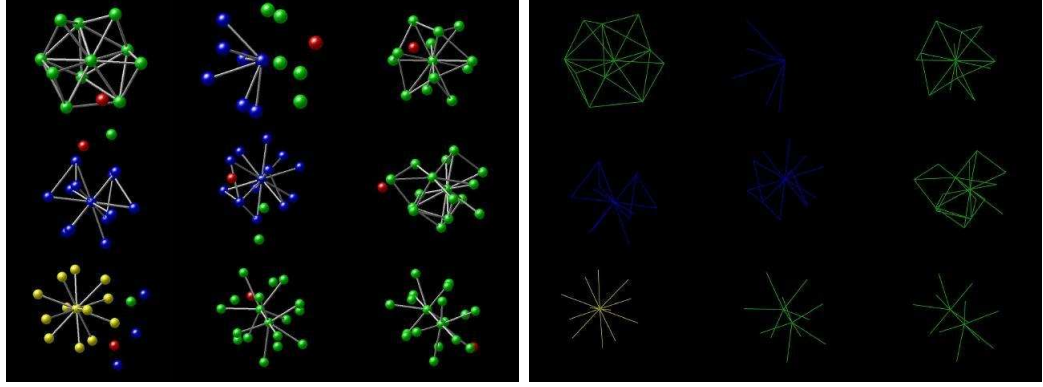


N=3, 4, 5, 6, 7, 8, 9, 10, 11 ([49, 39])

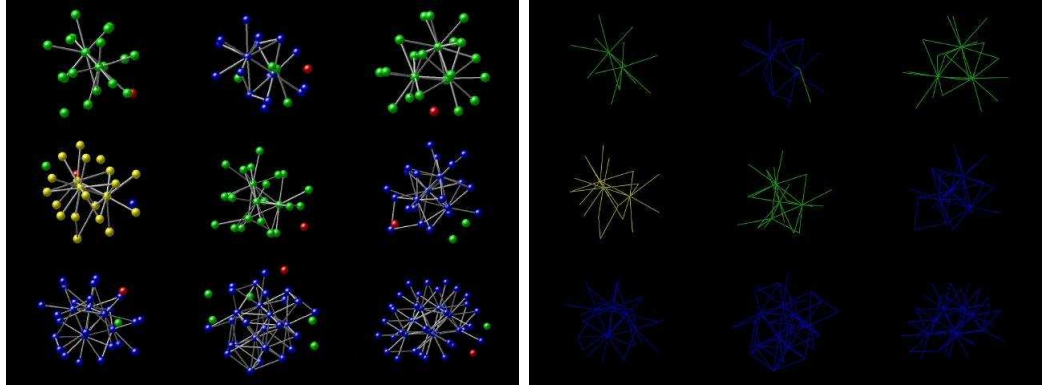


N=12, 13, 14, 15, 16, 17, 18, 19, 20 (ours)

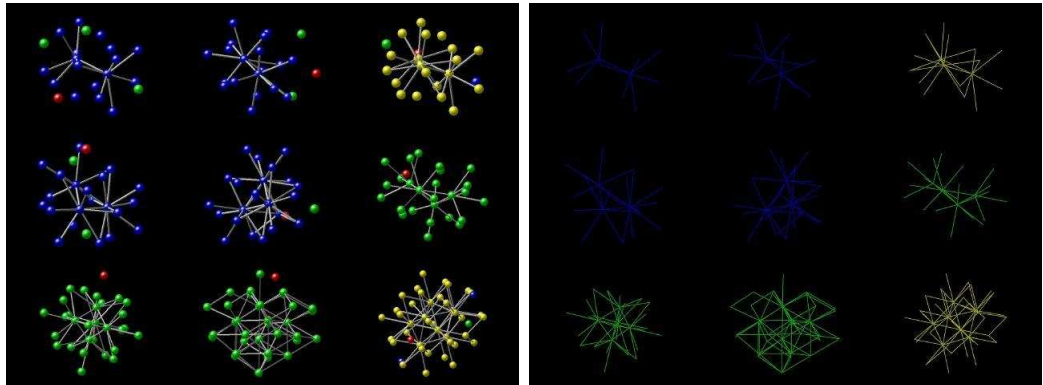




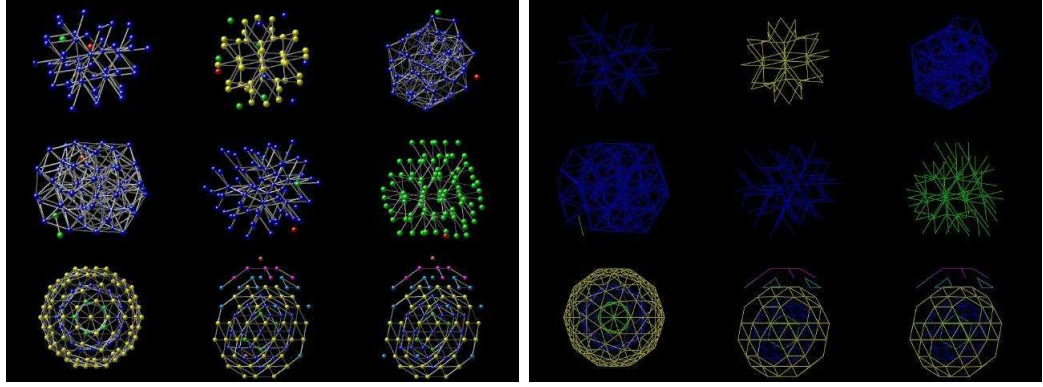
N=12, 13, 14, 15, 16, 17, 18, 19, 20 ([49, 39])



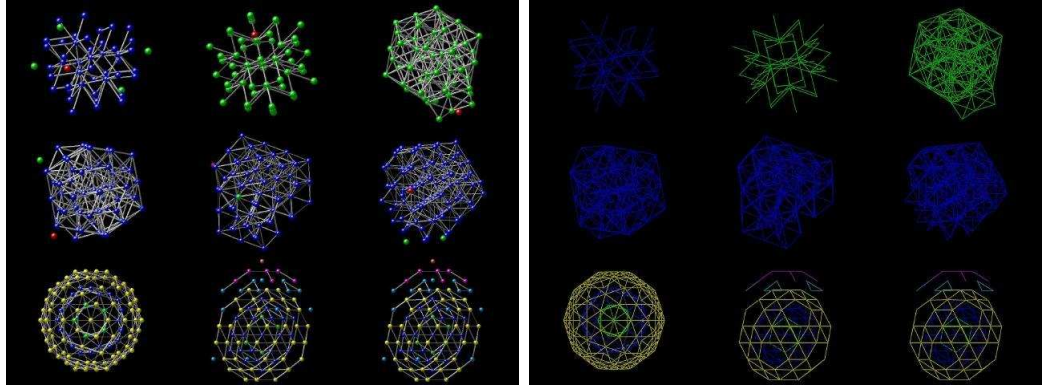
N=21, 25, 27, 30, 34, 44 (ours)



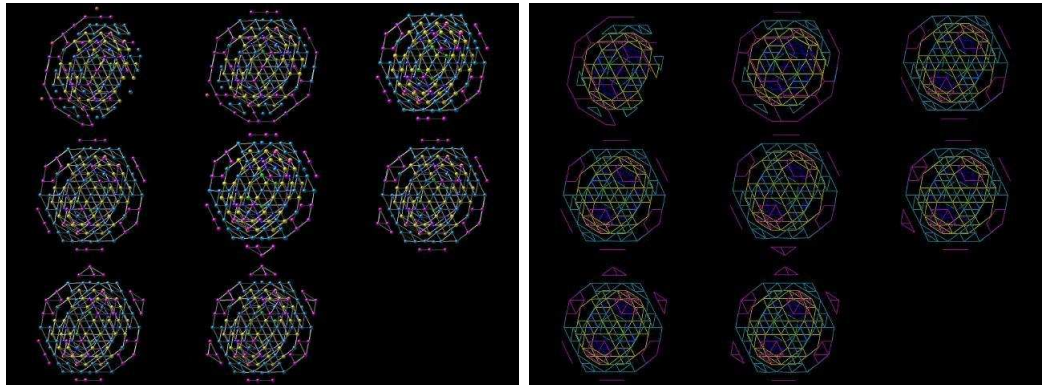
N=21, 25, 27, 30, 34, 44 ([49, 39])



$N=49, 56, 65, 67, 84, 93, 148, 170, 172$  (ours)



$N=49, 56, 65, 67, 84, 93, 148, 170, 172$  ([49, 39])



$N=268, 288, 293, 298, 300, 301, 304, 308$  (ours)

Table 1: Our numerical results for Lennard-Jones Protein Problem

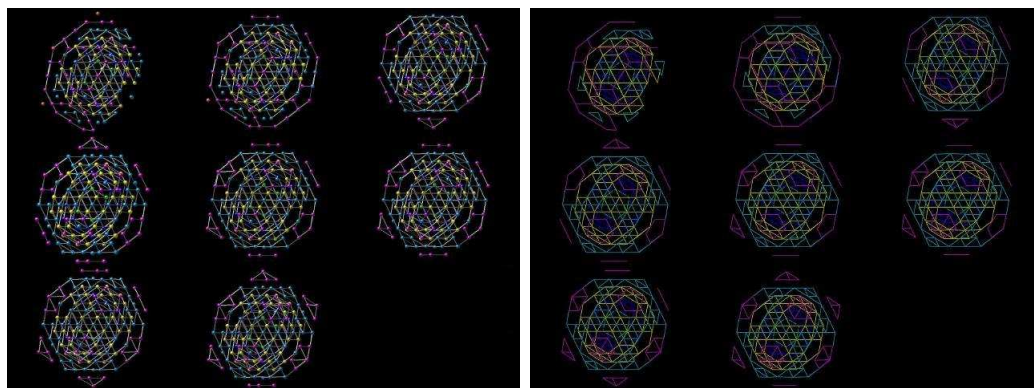
Number of atoms	Best value obtained	Best value known
19	-72.659782	-72.659782
20	-77.177043	-77.177043
21	-81.684571	-81.684571
22	-86.573675	-86.809782
23	-92.844461	-92.844472
24	-97.348815	-97.348815
25	-102.372663	-102.372663
27	-112.825517	-112.873584
30	-128.096960	-128.286571
34	-150.044528	-150.044528
44	-207.631655	-207.688728
49	-239.091863	-239.091864
56	-283.324945	-283.643105
65	-334.014007	-334.971532
67	-347.053308	-347.252007
84	-452.267210	-452.6573
93	-510.653123	-510.8779
148	-881.072948	-881.072971
170	-1024.791771	-1024.791797
172	-1039.154878	-1039.154907
268	-1706.182547	-1706.182605
288	-1850.010789	-1850.010842
293	-1888.427022	-1888.427400
298	-1927.638727	-1927.638785
300	-1942.106181	-1942.106775
301	-1949.340973	-1949.341015
304	-1971.044089	-1971.044144
308	-1999.983235	-1999.983300

## 4 Conclusions

In this paper, a brief review and a bibliography of important computational algorithms on minimizing the LJ potential energy are introduced in Sections 1 and 2. Section 3 of this paper illuminates many beautiful graphs for the three dimensional structures of molecules with minimal LJ potential.

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N=268, 288, 293, 298, 300, 301, 304, 308 ([49, 39])

## References

- [1] E. Aarts and J. Korst, *Simulated annealing and Boltzmann machines* (John Wiley and Sons, 1989).
- [2] L. Armijo, “Minimization of functions having continuous partial derivatives”, *Pacific J. Math.* **16** (1966) 1-13.
- [3] A. M. Bagirov, “Derivative-free methods for unconstrained nonsmooth optimization and its numerical analysis”, *Investigacao Operacional* **19** (1999) 75-93.
- [4] A. M. Bagirov, “A method for minimization of quasidifferentiable functions”, *Optimization Methods and Software*, **17**(1), 2002, 31-60.
- [5] A.M. Bagirov and A.M. Rubinov, “Cutting angle method and a local search”, to appear in *Journal of Global Optimization*.
- [6] A.M. Bagirov and J. Zhang, “Comparative analysis of the cutting angle and simulated annealing methods in global optimization”, to appear in *Journal of Optimization*.
- [7] D.G. Brooks and W.A. Verдини, “Computational experience with generalized simulated annealing over continuous variables”, *American Journal of Mathematical and Management Sciences* **8** (1988) 425-449.
- [8] V. Cerny, “Thermodynamical approach to the travelling salesman problem: an efficient simulation algorithm”, *Journal of Optimization Theory and Applications* **45** (1985) 41-51.
- [9] T. Coleman, D. Shalloway and Z. J. Wu, “A parallel build-up algorithm for global energy minimizations of molecular clusters using effective energy simulated annealing”, *J. Global Optimization* **4** (1994) 171-185.
- [10] A. Corana, M. Marchesi, C. Martini, and S. Ridella, “Minimizing multimodal functions of continuous variables with the simulated annealing algorithm”, *ACM Transactions on Mathematical Software* **13** (1987) 262-280.

- [11] D. M. Deaven, N. Tit, J. R. Morris and K. M. Ho, "Structural optimization of Lennard-Jones clusters by a genetic algorithm", *Chem. Phys. Lett.* **256** (1996) 195-200.
- [12] J. P. K. Doye, D. J. Wales and R. S. Berry, "The effect of the range of the potential on the structures of clusters", *J. Chem. Phys.* **103** (10) (1995) 4234-4249.
- [13] J. P. K. Doye and D. J. Wales, "Magic numbers and growth sequences of small face-centred-cubic and decahedral clusters", *Chem. Phys. Lett.* **247** (1995) 339-347.
- [14] J. P. K. Doye, D. J. Wales and M. A. Miller, "Thermodynamics and the global optimization of Lennard-Jones clusters", *J. Chem. Phys.* **100** (1998) 8143-8253.
- [15] J. Farges, M. F. de Feraudy, B. Raoult and G. Torchet, "Cluster models made of double icosahedron units", *Surf. Sci.* **156** (1985) 370-378.
- [16] D. L. Freeman and J. D. Doll, "Quantum Monte Carlo study of the thermodynamic properties of argon clusters: the homogeneous nucleation of argon in argon vapor and "magic number" distributions in argon vapor", *J. Chem. Phys.* **82** (1985) 462-471.
- [17] N. Gershenfeld, *The nature of mathematical modeling* (Cambridge University Press, 1999).
- [18] M. S. Gockenbach, A. J. Kearsley and W. W. Symes, "An infeasible point method for minimizing the Lennard-Jones potential", *Computational Optimization and Applications* **8** (3) (1997) 237-386.
- [19] B. Hartke, *J. Comp. Chem.* **20** (1999) 1752.
- [20] A.-R. Hedar and M. Fukushima, "Hybrid simulated annealing and direct search method for nonlinear global optimization", *Technical Report, Department of Applied Mathematics and Physics, Kyoto University* **2001-013** (December 2001).
- [21] A.-R. Hedar and M. Fukushima, "Simplex coding genetic algorithm for the global optimization of nonlinear functions", *Technical Report, Department of Applied Mathematics and Physics, Kyoto University* **2002-006** (March 2002).
- [22] M. R. Hoare, "Structure and dynamics of simple microclusters", *Advances in Chemical Physics* **40** (1979) 49-135.
- [23] M. R. Hoare and P. Pal, "Geometry and stability of "spherical" f.c.c. microcrystallites", *Nature (Physical Sciences)* **236** (1972) 35-37.
- [24] M. R. Hoare and P. Pal, "Statics and stability of small cluster nuclei", *Nature (Physical Sciences)* **230** (1971) 5-8.
- [25] M. R. Hoare and P. Pal, "Physical cluster mechanics: statics and energy surfaces for monatomic systems", *Advances in Chemical Physics* **20** (1971) 161-196.

- [26] M. R. Hoare and J. A. McInnes, “Morphology and statistical statics of simple microclusters”, *Adv. Phys.* **32** (1983) 791-821.
- [27] E. Horowitz and S. Sahni, *Data Structures in Pascal* (Computer Science Press, 1990).
- [28] R. Horst, P.M. Pardalos, and N.V. Thoai, *Introduction Optimization, Nonconvex Optimization and Its Applications* (Kluwer Academic Publishers, Dordrecht, 1995).
- [29] A.E.W. Jones and G.W. Forbes, “An adaptive simulated annealing algorithm for global optimization over continuous variables”, *Journal of Global Optimization* **6** (1995) 1-37.
- [30] S. Kirkpatrick, C.D. Gelatt, and M.P. Vecchi, “Optimization by simulated annealing”, *Science* **220** (1983) 671-680.
- [31] B. Leary, 2000: <http://www.sdsc.edu/RealPeople/leary.html>
- [32] R. H. Leary, “Global optima of Lennard-Jones clusters”, *Journal of Global Optimization* **11** (1997) 35-53.
- [33] M. Locatelli, “Simulated Annealing algorithms for continuous global optimization: convergence conditions”, *Journal of Optimization Theory and Applications* **104(1)** 121-133.
- [34] A. L. Mackay, “A dense non-crystallographic packing of equal spheres”, *Acta Crystallographica* **15** (1962) 916-918.
- [35] J. A. Northby, “Structure and binding of the Lennard-Jones clusters:  $13 \leq N \leq 147$ ”, *J. Chem. Phys.* **87 (10)** (1987) 6166-6177.
- [36] P. M. Pardalos, D. Shalloway and G. L. Xue, “Optimization methods for computing global minima of nonconvex potential energy functions”, *Journal of Global Optimization* **4** (1994) 117-133.
- [37] C. Reeves, *Modern heuristics for combinatorial optimization* (Wiley, 1995).
- [38] H.E. Romeijn and R.L. Smith, “Simulated annealing for constrained global optimization”, *Journal of Global Optimization* **5** (1994) 101-126.
- [39] D. Romero, C. Barron and S. Gomez, “The optimal geometry of Lennard-Jones clusters: 148-309”, *Computer Physics Communications* **123 (1-3)** (1999) 87-96.
- [40] A.M. Rubinov, *Abstract Convexity and Global Optimization* (Kluwer Academic Publishers, Dordrecht, 2000).
- [41] A.M. Rubinov and M. Andramonov, “Lipschitz programming via increasing convex-along-rays functions”, *Optimization Methods and Software* **10** (1999) 763-781.

- [42] J. Sun and J. Zhang, “Global convergence of conjugate gradient methods without line search”, *Annals of Operations Research* **103** (2001) 161-173.
- [43] D. J. Wales and J. P. K. Doye, “Global optimization by Basin-Hopping and the lowest energy structures of Lennard-Jones clusters containing up to 110 atoms”, *J. Phys. Chem. A* **101** (1997) 5111-5116.
- [44] L. T. Wille, “Minimum-energy configurations of atomic clusters: new results obtained by simulated annealing”, *Chem. Phys. Lett.* **133** (1987) 405-.
- [45] M. Wolf, *J. Phys. Chem. A.*, **102** (30) (1998).
- [46] G. L. Xue, “Improvement on the Northby algorithm for molecular confirmation: better solutions”, *Journal of Global Optimization* **4** (1994) 425-440.
- [47] G. L. Xue, “Molecular conformation on the CM-5 by parallel two-level simulated annealing”, *Journal of Global Optimization* **4** (1994) 187-208.
- [48] K.F.C. Yiu, Y. Liu, and K.L. Teo, “A hybrid descent method for global optimization”, to appear in *Journal of Global Optimization*.
- [49] <http://www-wales.ch.cam.ac.uk/~jon/structures/LJ/tables.150.html>
- [50] [http://www.vcl.uh.edu/~cbarron/LJ\\_cluster/LJpottable.html](http://www.vcl.uh.edu/~cbarron/LJ_cluster/LJpottable.html)
- [51] <http://shale.physics.gatech.edu/~matt/Public/ljfile.html>